



# The morphology and structure of natural clays from Yangtze River and their interactions with polyurethane elastomer



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## ABSTRACT

In thermoplastic polyurethane elastomer (PUE) technology, the necessity for revealing the interactions between clays and polyurethane chains is improving recently. In this paper, three different natural clays (NC) were firstly employed to prepare NC/PUE composites to explore the relation between fillers and PUE chains. We found that the natural clays were formed from sand to fertile soil, and then corroded deeply to CaCO<sub>3</sub> (rock) by surroundings, including water, wind and temperature and so on. Then, the neat PUE and NC/PUE composites were characterized by SEM, TEM, XRD, SAXS, FTIR and DSC to investigate the function of natural clays in polyurethane chains. We found that the different clays particles interacted with PUE chains in different ways. The lamellae and stacks of rock aggregated mainly in PUE matrix and interact with the hard/soft domains, while that of sand and soil aggregates mainly on the surface of PUE matrix.

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## 1. Introduction

Natural clay (NC) minerals are one of the most abundant compounds on earth with the characteristics of small size and the undergoing spontaneous modification and transformation with the change of environmental conditions, such as water, wind, sunshine and time. With the impact of these conditions, the crystalline structure, micro morphology and components (involving the elements of Si, Al, O, and Ca, sometimes Fe, Cu, etc.) of the NC vary in a wide range [1,2]. In the past decades, due to its excellent reinforcing function and low cost of clays, studies and applications of them as fillers in inorganic/organic matrix has been the main focus in asphalt [3,4], mortar, agriculture [5,6], ceramics, polymer [7–10] and water resources and hydropower engineering and so on [11,12]. One of the most successful and significant applications of NC is the concrete, whose main components are the silicate minerals. Thus, studies in the clays as fillers are significant and valuable. Recently, the academic and industrial attentions are paid on the silica/polymer micro- and nano-composites [10,13,14] due to the numerous potential applications of such inorganic/organic hybrid particles in photonic devices, bio-mimic materials, roofing

adhesives and smart Pickering emulsifiers [15,16]. Actually, the initial work of vinyl polymer-silica nanocomposites and of polyurethane-silicates nanocomposites were conducted by Barthelet et al. [17] and Zilg et al. [9] in 1999, respectively, and since then, various mixtures of polymer/inorganic particles and robust synthetic methods have been developed rapidly over the past decade or so. The natural clay are usually added as a reinforcing material to increase the thermal and abrasion resistance, as well as, tensile and tear strength of the polymer products [10,18].

Thermoplastic polyurethane elastomers (PUE) are polymers that bridge the gap between rubbers and plastics. Due to the copolymeric nature consisting on hard segments (HS) linked to soft segments (SS) in an alternative fashion, it is of interest to study the interaction mechanism between the NC and PUE for there may be interaction between the filler and hard domain, or soft domain, or both. In this way, the addition of the NC may have impact on the phase segregation or mixing, resulting in the variation of PUE properties. Thus, PUE with fillers of the NC can be tailored to meet the highly diversified demands of performance for application in building & construction, transportation, packaging, footwear, smart wearable equipment and appliances [19,20]. Although inorganic clays are popular used as fillers to reinforce mechanical properties of a polymer matrix in industrial practice, the origin of such mechanical reinforcement is confused and the function of the fillers in polymer matrix is still mysterious because most researches

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have been devoted to the improvement of various properties and application. As reported by Mishra et al. [21,22], Osman et al. [23], and Balmer et al. [15], the existence of the nano-fillers can interact with the PUE chains, inducing the segregation or mixing between hard and soft domains. Meanwhile, the surface modification for fillers may improve the degree of interaction between PUE domains and nanosilicate. However, the aggregation and dispersion of fillers in polymer are usually less concerned. Furthermore, most clays used as modifiers are obtained through synthesis route or complex modified processes instead of their initial state. In these ways, their dispersion and limited availability of nanowhiskers can be enhanced [9].

To the best knowledge of present authors, clays were seldom used in their initial state, or after facile handling, which may enhance the utilization efficiency of the abundant NC in wide areas. In this paper, the clays, obtained from nature, were firstly used to study the function of two phases in inorganic/organic composites to reveal the interaction mechanism between polyurethane chains and clays. We obtained the NC from Yangtze River of China to study their initial morphology and structure. And then, the natural clays were handled with easy and facile processes, such as mixing with water and HNO<sub>3</sub>, to exclude impurities. After that, the clays were directly mixed with PUE to study the aggregation and dispersion of the NC in PUE and the interaction between them. The filler dispersed in PUE may have multiple functions with the components due to the intrinsic complexity of PUE, such as hard domains, soft domains, and the microphase separation between them [24]. Thus, small-Angle X-ray scattering (SAXS) experiments were employed to explore the effect of the filler on the both phases of PUE.

## 2. Experiments

### 2.1. Materials

The diisocyanate used was 4,4-methylene-bis-(phenylisocyanate) (MDI, 98 wt% purity, purchased from Aladdin, Shanghai, China) which is crystal solid at room temperature. Polytetramethylene Ether Glycol (PTMEG, molecular weight ( $M_n$ ) = ca. 2000, purchased from Aladdin, Shanghai, China) was used as polyol oligomers to synthesize PUE (dried under vacuum at 120 °C before use), and ethyl alcohol, 1,4-butanediol (BDO, 99.5 wt% purity) were purchased from Fuchen Chemical Co., Ltd., Tianjin, China. Natural clays (NC) were collected from the bank of the Yangtze River. Nitric acid (HNO<sub>3</sub>, 65–68 wt%) was purchased from Sichuan XILONG Chemical Reagent Co., Ltd. China.

### 2.2. Physical processing of natural clay

All the three kinds of natural clays collected from the bank of Yangtze River were processed in a way as follows. Firstly, they were dried in an oven at 50 °C for 48 h, and then the clay was put through 60 mesh sieves to exclude sundries in large size. Secondly, the sieving clay was smashed with a pulverizer (JP-250A-2, Shanghai JIUPIN DIANQI) at a high speed of 29,000 r/min for 10 min. Then, the clays were put through 120 mesh sieves to obtain the sieving clays, which was followed by putting into sample bottle with deionized water, dispersing with ultrasonic for 15 min, and distilling at room temperature for 48 h to exclude water soluble sundries and suspended solids. Afterwards, the clays were dried thoroughly in an oven at 50 °C. The dried clays were milled by the ball mill (QM-3SP4, Nanjing NanDa Instrument Plant) with ethyl alcohol as solvent with agate grinding balls in different sizes for 4 h. After then, the clay powders was washed with deionized water and dried thoroughly at 50 °C. The dried powders were

put through 200 mesh sieves and the sieving clays were obtained, after that, they were put into sample bottle with deionized water again, distilling for two weeks. The precipitates were collected and dried thoroughly at 50 °C.

### 2.3. Purification of natural clay powders

The clay was purified by ultrasonically dispersing it in mixture of deionized water and HNO<sub>3</sub> for 30 min, and then the mixture of clay and HNO<sub>3</sub> (5 mol/L) was stirred at 60 °C for 12 h in a reflux unit. Afterwards, the solution was diluted and rinsed by deionized water under a centrifuge (Cence H1850, XiangYi, Hunan, China) with the 6000 r/min for several times until the pH value (detected by PHS-3C Digital Display Acidity Meter (Hangzhou LEICI Analytic Factory China.) with an E-201-9 pH Combination Electrode from Shanghai Ruosull Science and Technology Co., Ltd. China reaches neutral, and then dried thoroughly in vacuum at 50 °C for further use.

### 2.4. Preparation of PUE/natural clay composites

To evaluate the interaction between the inorganic natural clay and polymer chains, polyurethane elastomer is synthesized due to the highly sensitive to chemical and physical structure of the materials and versatile properties easily analyzed [19]. The samples were prepared with 30% hard segment content (HSC) by a two-step polymerization, in which the oligomer polyols react with the diisocyanate to obtain the prepolymer of PUE initially and the prepolymer react with the mixture of chain extender and clays secondly. The polymerization reactions were conducted in a 150 mL three-necked, round bottom, Pyrex reaction flasks equipped with an overhead stirrer (FLUKO R30, Shanghai), and addition funnel and nitrogen inlet. Firstly, the PTMEG was dried in an oven at 120 °C with a vacuum of –0.05 MPa for 2 h. Secondly, the calculated amounts of diisocyanate and dried PTMEG oligomer were introduced into the flasks with slowly stirring and heating to 50 °C in the thermostat water bath for 1 h, and then the temperature increased to 80 °C for 30 min. Thirdly, the purified clay was sonicated in a water bath for ~30 min prior to mixing with a stoichiometric amount of chain extender (BDO), introduced into the addition funnel and slowly added into the flasks to promote the chain extension step under a stirring speed of 600 rpm for ~3 min. The resulting mass was then transferred to a Teflon plate mold and cured for 4 h at 70 °C. Then the composites were cured for 24 h at 100 °C. Lastly, the structure and some properties of natural clay/polyurethane elastomer (NC/PUE) composites were detected by various methods to study the interaction between the polymer chains and silicates.

### 2.5. Characterization and property measurements of NC and NC/PUE

Fourier transform infrared spectroscopy (FTIR) was used to identify the structure of NC and NC/PUE. The infrared spectra of the dried polyurethane films were obtained using a Fourier transform IR spectrophotometer (SHIMADU FTIR-8400S (CE)) and recorded in the transmission mode at room temperature by averaging 20 scans at a resolution of 16.0 cm<sup>-1</sup>. The spectra were analyzed in the frequency range of 4000–400 cm<sup>-1</sup>. Differential scanning calorimetry (DSC) experiments were carried out in NETZSCH DSC 200 F3 Maia<sup>®</sup> with a temperature range from –100 to 150 °C at a heating and cooling rate of 10 °C/min under a N<sub>2</sub> atmosphere (flow rate: 30 mL/min). The samples weights were about 5–10 mg. In order to minimize effects of thermal history, first heating process from room temperature to 150 °C was performed, and then all the samples were kept at 150 °C for 5 min, and then two consecutive runs were carried out: (1) Cooling from

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